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Method of making a moisture-curable silicon terminated polymer.

57

The method comprises reacting a polyurethane prepolymer having terminal active hydrogen atoms with an isocyanato organosilane having a terminal isocyanate group and at least one hydrolyzable alkoxy group bonded to silicon. The moisture-curable polymer obtained by this method can advantageously be used in sealant compositions. The polymer presents a very rapid cure rate in the presence of moisture, and it is stable under unhydrous conditions.

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METHOD OF MAKING A MOISTURE-CURABLE SILICON TERMINATED
POLYMER

The present invention relates to a method of making a moisture-curable silicon terminated polymer, to the moisture-curable silicon terminated polymer made by the method, and to a moisture-curable sealant
5 composition comprising the moisture-curable polymer.

U.S. Patent 3 632 557 Brode et al., teaches silicon terminated organic polymers which are curable at room temperature in the presence of moisture. The patent teaches that such polymers, particularly after
10 the inclusion therein of fillers which are conventional for incorporation into elastomeric compositions, can be used for coating, caulking, and sealing.

Indeed, U.S. Patent 3 979 344 Bryant et al., and U.S. Patent 4 222 925, Bryant et al., teach sealant compositions, curable at room temperature in the presence of moisture, comprising the organosilicon polymers of the Brode et al. patent in combination with specific additive materials. Thus, the first
15 of the Bryant et al. patents teaches the addition of N-(beta-aminoethyl)-gamma-aminopropyltrimethoxy silane to a sealant composition containing such a silicon terminated organic polymer, and the second of the aforementioned Bryant patents relates to the inclusion of a particular carbon black filler in
20 such compositions. These patents teach the utility of the silicon terminated organic polymers, or of sealant compositions containing the same, for forming tenacious bonds to non-porous surfaces, particularly glass.

30 The silicon terminated organic polymers of the present invention are similarly moisture-curable at room temperature and can similarly be formulated into sealant compositions comprising fillers and

other additives. As do the prior art materials, the polymers and compositions of the present invention show particularly good adhesion to non-porous surfaces such as glass and are particularly characterized by a very rapid cure rate which facilitates the use of the polymers and sealant compositions compounded therewith in industrial applications, for example as sealants for automotive glass such as windshields.

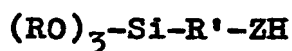
10 The silicon terminated organic polymers of the Brode et al. patent are prepared by reacting a polyurethane prepolymer having terminal isocyanate groups with a silicon compound containing alkoxysilane groups and having a mercapto group or a primary
15 or secondary amino group reactive with isocyanate groups. Upon reaction of the mercapto or amino group with the terminal isocyanate groups of the polyurethane prepolymer, a moisture-curable polymer having terminal hydrolyzable alkoxysilane groups is formed.
20 These terminal alkoxysilane groups, in the presence of atmospheric moisture, react to form siloxane (-Si-O-Si-) groups, possibly by way of intermediate silanol formation. The formation of the siloxane linkages not only crosslinks and cures the moisture-
25 -curable polymer, but also promotes adhesion of the polymer to non-porous surfaces such as glass surfaces, with which the hydrolyzable alkoxysilane groups form particularly tenacious bonds in the presence of atmospheric moisture.

30 The prior art silicon terminated polymers require relatively long curing times in the presence of moisture; they usually gel in about 4 hours when exposed to atmospheric moisture. On the other hand the stability of these polymers is not entirely satisfactory, the polymers have a great tendency to skin
35 on storage even under unhydrous conditions.

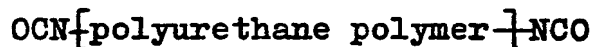
The present invention is therefore aimed at

providing a novel method resulting in a silicon terminated polymer having improved properties, such as higher curing speed and better stability.

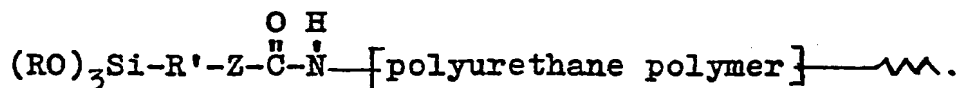
According to the present invention, a polyurethane prepolymer is also reacted with an organosilane compound having one or more hydrolyzable alkoxy-silane groups. However, according to the invention, the polyurethane prepolymer has terminal active hydrogen atoms, present in groups such as hydroxy groups, mercapto groups, or primary or secondary amino groups. These active hydrogen atoms are reacted with an isocyanate group present in the organosilane compound. As in the prior art, urethane, thiourethane, or urea groups are produced by the reaction, but the nature in which these linking groups bond the terminal alkoxy-silane groups to the polyurethane prepolymer differs from that known in the prior art and accounts for the improved properties of the claimed polymers and sealants. By way of illustration, the Brode patent shows the reaction of a compound of the formula



where R is lower alkyl, R' is a divalent bridging radical, and Z is S or NR" where R" is H or lower alkyl, with an isocyanato-terminated polyurethane polymer of the formula

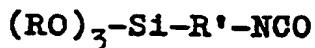


The reaction of the two compounds produces a polyurethane polymer having the following terminal group:

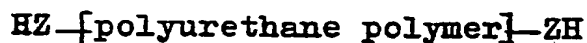


In contrast, according to the present invention, an isocyanato terminated organosilane compound, for

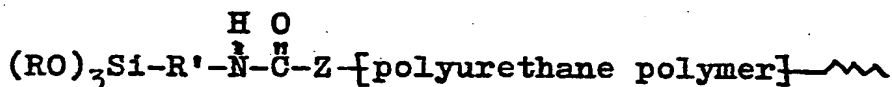
example



- 5 is reacted with a polyurethane prepolymer having active hydrogen terminals, e.g.



- 10 where Z is O, S, or NR" and R" is H or lower alkyl, whereby a polymer terminal group of the structure



- 15 is formed.

The Brode et al. patent teaches in detail the production of isocyanato terminated polyurethane polymers by the reaction of an organic polyisocyanate with a polyhydroxy compound. In the reaction, the

20 polyisocyanate is employed in a molar excess so that the resultant polymers have isocyanate terminals. Exactly the same compounds and reagents may be used according to the present invention to form the prepolymers of interest, except that the hydroxy compounds are used in a molar excess with respect to

25 the polyisocyanate so that the resulting reagents have hydroxy terminals. Exactly the same polyols may be employed as in the prior art, e.g. polyester polyols including lactone polyols prepared by the polymerization of lactones, particularly alkanolactones

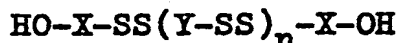
30 such as epsilon-caprolactone, compounds such as castor oil, and particularly, polyether polyols. The polyether polyols may be prepared by forming alkylene oxide adducts of the polyester polyols and lactone polyols

35 discussed immediately above, or by reaction of alkylene oxides with materials such as castor oil. However, the preferred polyether polyols are polyoxal-

kylene polyols, e.g. polyoxyalkylene diols prepared, for example, by the homopolymerization or copolymerization of materials such as ethylene oxide and propylene oxide. Polyoxyalkylene triols, for example
 5 linear compounds having pendant hydroxy groups or having branched polyether chains, may be employed as starting compounds in admixture with diols.

Further suitable polyols are polyhydroxy polysulfide polymers of the formula

10



wherein X and Y are each divalent aliphatic groups and n has a value between 1 and 100.

15

Polyurethane prepolymers having terminal mercapto groups are obtained by an analogous reaction between a polyisocyanate and thio compounds analogous to the polyester and polyether compounds discussed immediately above. In similar fashion, polyurethane prepolymers having terminal amino groups
 20 are prepared by the condensation reaction of polyisocyanates with polyamines, e.g. diamines and triamines, having primary and/or secondary amino groups therein.

25

The use of prepolymers prepared from polyols is preferred according to the present invention. Such polyols, having two or more hydroxyl groups, generally have a molecular weight between 500 and 6000 and can be either polyester or polyether polyols,
 30 with the latter being preferred. The polyols or polyol mixtures used according to the invention generally have hydroxyl equivalent weights between 50 and 2000. Preferred polyoxyalkylene polyols, e.g. polyoxypropylene, have hydroxyl equivalent weights between
 35 200 and 2000.

As mentioned earlier, a portion of the diols which are usually employed in the reaction with poly-

isocyanates can be replaced by a triol, leading to the formation of branched polyurethane prepolymers.

A further preferred embodiment according to the present invention is the replacement of some of the polyol compound or mixture of polyols with water. The water, on reaction with isocyanate, releases carbon dioxide and forms an amino group. The latter in turn reacts with further isocyanate groups to form urea groups. According to the present invention it has been found that the resulting prepolymers containing both urethane and urea groups have improved heat stability and weathering resistance. While the applicant does not wish to be bound by theory, it is possible that the synergistic presence of urea and urethane groups in the prepolymer lengthens the induction period which precedes the initiation of the degradation of polyurethane polymers by heat and weathering phenomena such as exposure to ultraviolet light.

In this embodiment, up to 25 percent of the equivalents of isocyanate-reactive OH groups contributed by the polyol may be replaced by an equal number of equivalents of water. Preferably, the polyol employed in this embodiment is an aliphatic polyol such as a polyoxyalkylene polyol.

The organic polyisocyanates employed according to the present invention for formation of the prepolymers having terminal active hydrogen atoms are those also used in the Brode et al. patent. That is, they are aliphatic, cycloaliphatic, araliphatic, or aromatic polyisocyanates, suitably di- and/or tri-isocyanates. Particularly preferred materials for use according to the present invention are 4,4-diphenylmethane diisocyanate having aromatic characteristics, the cycloaliphatic diisocyanate 3-isocyanatomethyl-3,5,5-trimethyl cyclohexyl isocyanate known

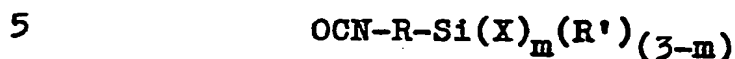
as isophorone diisocyanate, and dicyclohexyl-4,4'-methane diisocyanate, commercially available under the tradename "Hylene W". Mixtures of two or more of these preferred materials are also preferred for
5 use in the present invention.

The reaction of the polyurethane with a polyol, polythiol, or polyamine may be suitably carried out in the presence of a catalyst. For the formation of urethanes, for example, the stannous salts of car-
10 boxylic acids, such as stannous octoate, stannous oleate, stannous acetate, and stannous laurate are known as such catalysts. Further, dialkyltin dicarboxylates such as dibutyltin dilaurate and dibutyltin diacetate are known in the art as urethane cata-
15 lyst, as are tertiary amines and tin mercaptides. Still other catalytic materials are known to those skilled in the art. The amount of catalyst employed is generally between 0.005 and 5 percent by weight of the mixture catalyzed, depending on the nature of
20 the isocyanate.

Suitable conditions for such reactions are well known in the art. For example, the ingredients are reacted at a temperature between 0°C and 120°C, preferably between 25°C and 90°C, until no further
25 isocyanate can be detected by infrared analysis. The reactions are carried out under an inert atmosphere, such as a nitrogen blanket, and under anhydrous conditions.

The resultant prepolymers having terminal
30 groups with active hydrogen atoms have molecular weights varying between 3000 and 18000. Preferred prepolymers having a molecular weight between 10,000 and 15,000 have a moderate viscosity which facilitates their further reaction with the isocyanato organo-
35 silane compounds used to "cap" the prepolymers and which also facilitates the compounding of the final "capped" materials into sealant compositions.

The organosilane compounds which are reacted with the prepolymers discussed above preferably have the formula



wherein R is a divalent organic group, R' is hydrogen or alkyl having 1 to 4 carbon atoms, for instance, X is a hydrolyzable alkoxy group having from 1 to 4
10 carbon atoms, for instance, and m is an integer from 1 to 3. Group R can have any of a wide variety of structures forming a stable bridge between the terminal isocyanate group and the alkoxysilane group. A number of structures for such isocyanato alkoxysilane
15 compounds are illustrated, for example, in columns 4 and 5 of U.S. Patent 4 146 585. Preferably, however, R is a lower alkyl group having at least 3 carbon atoms therein, and particularly preferred materials for use according to the present invention are gamma-
20 -isocyanatopropyl-triethoxy silane and gamma-isocyanato-propyl-trimethoxy silane.

When the polyurethane prepolymer having active terminal hydrogen atoms is reacted in an approximately stoichiometric amount with an isocyanato alkoxysilane
25 like that described above, the isocyanate groups of the latter reagent react with an equivalent amount of terminal active hydrogen atoms of the prepolymer to form a stable prepolymer having terminal alkoxy-silane groups. The number of alkoxysilane groups pre-
30 sent in the system will determine the degree of cross-linking of the polymer when it is cured by exposure to moisture such as atmospheric moisture.

The reaction between the prepolymer and the isocyanato alkoxysilane is carried out under anhydrous
35 conditions and preferably under an inert atmosphere, such as a nitrogen blanket, to prevent premature

hydrolysis of the alkoxysilane groups. The reaction is suitably carried out between 0°C and 150°C, preferably between 25°C and 80°C, until isocyanate groups can no longer be detected by infrared analysis.

5 As mentioned earlier, on exposure to moisture, for example atmospheric moisture, the alkoxysilane groups will hydrolyze, possibly with intermediate formation of the corresponding silanol, and will eventually form siloxane (-Si-O-Si-) bonds which lead to
10 curing and bonding of the material to a substrate such as glass.

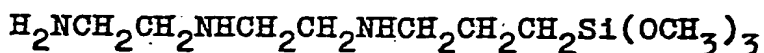
The rate of hydrolysis of the alkoxysilane by moisture, and consequently the rate of crosslinking, is accelerated by the use of catalysts known
15 to promote the condensation of silanols. These materials include metal salts, such as tin salts, of carboxylic acids, organosilicon titanates, alkyltitanates, and the like. Dibutyltin diacetate is a preferred catalyst according to the present invention
20 and is preferably employed in an amount between 0.1 and 1 percent by weight of the polymer, preferably between 0.2 and 0.6 percent by weight. Accordingly, such catalysts are suitably present in sealant compositions comprising the polymer of the invention as
25 a component therein.

It has further been found that the presence of a quaternary arylalkyl or aralkylalkyl ammonium compound, particularly a quaternary ammonium hydroxide such as benzyl trimethyl ammonium hydroxide,
30 surprisingly and unexpectedly accelerates curing of the polymers of the present invention, and such materials are suitably incorporated into sealant compositions comprising or consisting of the polymer of the invention. A rapid cure mechanism is of particular importance, for example, when quick adhesion
35 of a composition containing the polymers of interest, such as a sealant composition, to parts to be

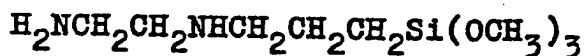
assembled with the sealant is required. Such a rapid cure is an important factor, for example, during the assembly and mounting of glass windshields in the automotive industry.

5 For formulation in sealant compositions, the polymers of the present invention are combined with fillers and additives known in the prior art for use in elastomeric compositions. By the addition of such materials, physical properties such as viscosity, flow rate, sag, and the like can be modified. To prevent premature hydrolysis of the moisture-sensitive groups of the polymer, the fillers should be thoroughly dried before admixture therewith. Exemplary filler materials and additives include materials such as carbon black, titanium dioxide, clays, calcium carbonate, surface treated silicas, ultraviolet stabilizers, antioxidants, and the like. This list, however, is not comprehensive and is given merely as illustrative.

20 As mentioned earlier, a monomeric alkoxy silane, preferably a monomeric amino alkoxy silane, is suitably physically incorporated together with the polymer in sealant compositions of this type. On hydrolysis, the monomeric alkoxy silane functions as a further cross-linking agent between the polymer molecules and/or between the polymer molecules and a surface, such as a glass surface, onto which the sealant compositions may be applied. In particular, N-alkyl-aminoalkyl trialkoxy silane monomers are suitably optionally added as such supplementary crosslinking agents, particularly those compounds in which the alkyl groups are all lower alkyl groups having 1 to 4 carbon atoms. Particularly preferred crosslinking agents are N-(beta-aminoethyl), N'-(gamma-trimethoxysilyl propyl)-ethylenediamine of the formula



and N-(beta-aminoethyl)-gamma-aminopropyl trimethoxy-silane of the formula



5

The latter is the same compound taught to be useful as an additive to sealants in U.S. Patent 4 222 925 mentioned earlier herein.

10 As mentioned earlier, the presence of a quaternary ammonium compound, particularly of a quaternary ammonium hydroxide, greatly accelerates the cure rate of the polymers according to the present invention and sealant compositions containing the same. These accelerators are preferably present in the com-
15 positions in an amount between 0.1 and 5 percent by weight of the polymer being cured.

The use of quaternary ammonium compounds, including hydroxides, as catalysts for the curing of organopolysiloxane resins is known in the art. For
20 example, U.S. Patent 2 759 007 to Dunham et al. discloses the formation of low molecular weight polysiloxanes by the hydrolysis and condensation of, for example, dialkyl dialkoxy silanes. As disclosed in the patent, dialkylcyclosiloxanes comprising three
25 to five monomer units make up a large portion of the resulting product. These oligomeric cyclic siloxanes are difficult to condense or polymerize into higher molecular weight materials. However, alkaline catalysts, including quaternary ammonium hydroxides, are
30 taught to facilitate this reaction. The reaction, however, has no pertinence to the hydrolysis of alkoxy-silanes initially to form polymeric organosilanes, possibly by way of an intermediate silanol.

U.S. Patent 3 208 972 to Lyons discusses a
35 method of making monomethylsiloxane by the hydrolysis of methyltrimethoxy silane or methyltriethoxy-silane in the presence of an alkaline material, in-

cluding quaternary ammonium hydroxides. However, the reaction is limited to hydrolysis of these monomers, is limited to the formation of a siloxane polymer comprising a repeating $\text{CH}_3\text{SiO}_{3/2}$ unit, and must
5 be carried out in water. At least 6 mols of water per mol of the initial silane are necessary to produce the siloxane product in this patent.

A better understanding of the present invention and of its many advantages will be had by referring to the following specific Examples, given
10 by way of illustration. In the following Examples, the polyether diol employed, unless otherwise indicated, is a polyoxypropylene diol having an average molecular weight of about 2,000 and commercially
15 available under the tradename "Pluracol P 2010". Unless otherwise indicated, references in the Examples to a polyether triol are to a polyoxypropylene triol having an average molecular weight of about 4,000 and commercially available under the tradename "Pluracol TPE-4542". The triol is prepared by the polymeri-
20 zation of propylene oxide onto a trihydric starting material such as glycerine or trimethylol propane. Unless otherwise indicated, the isocyanatoalkoxy silane employed in the Examples is gamma-isocyanato-
25 propyl triethoxysilane.

Example 1

A silane-terminated prepolymer having a linear polyether structure is prepared by mixing thoroughly
30 343.5 g (0.343 equivalent) of polyether diol, 36.0 g (0.286 equivalent) of 4,4'-diphenylmethanediisocyanate, and 0.02 g of dibutyltin dilaurate as a catalyst in a reaction vessel in the presence of a very small quantity of a defoaming agent. Because of re-
35 action of the isocyanate and hydroxyl groups, the temperature of the mixture may rise to as high as 45°C during mixing. The temperature then is raised to 75°C

and maintained for about 3 hours until isocyanate can no longer be detected therein by infrared spectroscopy.

5 Thereafter, 14.1 g (0.057 equivalent) of isocyanatoalkoxy silane are added and the reaction temperature is again kept at 75°C for about three hours until no isocyanate can be detected in the reaction mixture.

10 The prepolymer is then filled into a metal can container, degassed, flushed with nitrogen, and stored for further compounding.

Example 2

15 A silane terminated prepolymer was synthesized by mixing thoroughly 389.2 g (0.77 equivalent) of a polyoxytetramethylene diol commercially available under the tradename "Polymeg 1000" (m.W. \approx 1000),
20 76.9 g (0.62 equivalent) of 4,4'-diphenylmethane diisocyanate, 57.4 g of toluene, and 0.02 g of dibutyltin dilaurate as a catalyst in a reaction vessel. The mixed ingredients were then heated at 75°C for three hours or until isocyanate groups could no longer be detected in the reaction mixture. Finally
25 38.0 g (0.15 equivalent) of isocyanato-alkoxysilane were added. The mixture was again kept at 75°C for six hours until NCO could not be detected by infrared analysis. The prepolymer was then emptied into a metal can container, degassed, flushed with nitrogen
30 and stored.

Example 3

35 A polymer containing a polyurethane backbone terminated with gamma-isocyanatopropyl trimethoxysilane, instead of gamma-isocyanatopropyl triethoxysilane as in the previous examples, was prepared by thoroughly mixing 283.0 g (0.15 equivalent) of a

polyether diol having an hydroxyl equivalent weight of 1840 and commercially available under the trade-name "Olin Poly-G-55-30", 9.6 g (0.077 equivalent) of 4,4'-diphenylmethane diisocyanate, 0.02 g of di-
 5 butyl tin dilaurate as a catalyst and heating at 75°C for three hours until no isocyanate absorption was observed in an infrared spectrum. Then 15.8 g (0.07 equivalent) of gamma-isocyanatopropyl trimethoxy-
 10 silane were added and the whole mixture was again heated at 75°C for five hours until isocyanate groups could no longer be detected by infrared analysis. The prepolymer was placed in a metal can container, degassed, flushed with nitrogen and stored for further compounding.

15

Example 4

A silane terminated polyester prepolymer was prepared by mixing thoroughly 745.5 g (7.78 equivalents) of a polycaprolactone diol having an hydroxyl
 20 equivalent weight of 267 and commercially available under the tradename "PCP-0200", 322.4 g (2.55 equivalents) of 4,4'-diphenylmethane diisocyanate, and 183.0 g of toluene in a reactor. The mixed ingredients were then heated at 75°C for three hours until iso-
 25 cyanate groups could not be detected in the reaction mixture. Finally 57.5 g (0.23 equivalent) of gamma-isocyanatoalkoxysilane were added. The mixture was once more kept at 75°C for 8 hours until no isocyanate absorption could be observed in an infrared spectrum.
 30 The prepolymer was then emptied into a metal can container, degassed, flushed with nitrogen and stored.

Example 5

A silane terminated branched polyether pre-
 35 polymer was prepared by combining 12024 g (12 equivalents) of polyether diol and 1764 g (14 equivalents) of 4,4'-diphenylmethane diisocyanate in a reaction

vessel together with 6036 grams of a mixed plasticizer comprising 310 grams of an alkylnaphthalene monomer and 5726 g of a C₇-C₁₁-dialkylphthalate. The combined ingredients were heated to 63°C, heating was
 5 terminated, and 4 g of triethylene diamine catalyst were added. The temperature of the reaction mixture was then brought to 75°C and kept at this value for ten hours. The NCO content was found to be 0.42 percent, equal to the theoretical value. At this
 10 point, 9084 g (6 equivalents) of polyether triol and a further 14 g of triethylene diamine catalyst were added to the reaction mixture. A temperature of 55°C was maintained for three hours, at which time no isocyanate could be detected by infrared spectroscopy.
 15 Finally, 988 g (4 equivalents) of isocyanatoalkoxysilane and a further 4 g of triethylene diamine catalyst were added. The resulting mixture was brought to a temperature of 75° - 80°C and kept at this temperature for an additional three hours or
 20 until no isocyanate content was detectable.

The prepolymer was then filled into a metal can container, degassed, flushed with nitrogen, and stored.

25 Example 6

A silane terminated branched polyether prepolymer was synthesized by combining 182.2 g (0.18 equivalent) of polyether diol, 26.7 g (0.21 equivalent) of 4,4'-diphenylmethane diisocyanate, and 91.5 g of
 30 a C₇-C₁₁-dialkyl phthalate in a reaction kettle together with 0.24 g of triethylene diamine as a catalyst and a small quantity of a defoaming agent. The reaction mixture was heated at 75°C for about 8 hours. The NCO content was found to be 0.42 percent,
 35 equal to the theoretical value. Then 149.5 g (0.09 equivalent) of a polyether triol prepared from glycerine and propylene oxide, having an hydroxyl equi-

valent weight of 1644 and commercially available under the tradename "Pluracol 816", and 0.12 g of triethylene diamine catalyst were added to the reaction mixture. A temperature of 55°C was maintained
5 for three hours or until no isocyanate groups could be detected by infrared analysis. Finally, 15.0 g (0.06 equivalent) of gamma-isocyanato-alkoxysilane was added. The whole mixture was heated to 75°C and kept at this temperature for an additional 6 hours
10 until no isocyanate content was detectable. The prepolymer was then emptied into a metal can container, degassed, flushed with nitrogen, and stored.

Example 7

15 The following polymer has a linear polyether backbone and contains aliphatic urethane linkages together with urea groups.

416.6 g (3.75 equivalents) of isophorone diisocyanate were heated to 95°C and then combined
20 with 0.75 g of a surfactant, 0.08 g of dibutyltin dilaurate catalyst, and 0.02 g of triethylene diamine as a catalyst. After thorough mixing, 8.5 g (0.94 equivalent) of water were added dropwise to the mixture at a rate about one drop every ten seconds.
25 During the addition of water, the temperature of the mixture was kept at 95°C.

When water addition was complete, heating was stopped and the reaction mixture was slowly cooled to room temperature with stirring. The product had
30 an isocyanate content of 29.1 percent, compared with a theoretical value of 27.8 percent. (The high value of NCO may be due to loss of water during the reaction).

Based on the isocyanate content so determined, the number of equivalents of reaction mixture was
35 calculated and 3606.5 g (3.51 equivalent) of polyether diol were added to provide a slight excess of hydroxy groups with respect to NCO. At the same time, 0.38 g

of dibutyltin dilaurate catalyst were added to the mixture, which was then heated to 75°C and maintained at this temperature for 8 hours until isocyanate could no longer be detected in the reaction mixture.

5 Finally, 172.9 g (0.70 equivalent) of isocyanato-alkoxysilane were added. The mixture was again kept at 75°C for eight hours until NCO could no longer be detected.

10 The prepolymer was then filled into a metal can container, degassed, flushed with nitrogen, and stored for further compounding.

Example 8

15 An alkoxysilane terminated polymer similar to that of Example 7 and comprising a linear polyether structure having both urea and aliphatic isocyanate groups therein was prepared by heating 1194.7 g (9.13 equivalents) of dicyclohexyl-4,4'-methane diisocyanate to 95°C in a reaction vessel. 2.0 gram
20 of a surfactant ("Igepal"), 0.2 g of dibutyltin dilaurate catalyst, and 0.5 g of triethylene diamine catalyst were added. Next, 10.4 g (1.13 equivalents) of water were added dropwise at the rate of about one drop every ten seconds. During the addition of
25 water, the pot temperature was kept at 95°C. When addition was completed, heating was stopped and the reaction mixture was slowly cooled to room temperature with stirring. The resultant reaction product had an isocyanate content of 28.7 percent, from which
30 the equivalent weight of the reaction mixture was calculated to be 146.4.

35 10108.1 g (10 equivalents) of polyether diol were added to the mixture together with 0.16 g of dibutyltin dilaurate catalyst. The mixture was heated to 75°C and maintained at this temperature for 16 hours or until isocyanate could any longer be detected in the reaction mixture. Since the diol is used

in slight excess, the resulting product is hydroxy terminated.

Now, 494.0 g (2 equivalents) of isocyanato-alkoxy silane and 0.16 g of anti-foaming agent were added and the mixture was again kept at 75°C for a further six hours or until no isocyanate can be detected.

The resulting prepolymer was filled into a metal can container, degassed, flushed with nitrogen, sealed and stored for further compounding.

Example 9

A polymer having a polyether structure comprising ureagroups and aliphatic urethane groups therein and further comprising four ethoxysilane terminal groups per molecule was synthesized as follows.

An adduct containing urea groups was prepared by reacting isophorone diisocyanate and water in the presence of a surfactant, of dibutyltin dilaurate, and of triethylene diamine as earlier described in Example 7. 27.0 g (0.93 equivalent) of this adduct were then combined with 162.3 g (0.80 equivalent) of a polyether diol, 0.04 g of dibutyltin dilaurate catalyst, 0.02 g of an anti-foaming agent, 4.1 g of an alkylnaphthalene plasticizer, and 81.2 g of a C₁₇-C₁₁-dialkylphthalate plasticizer in a 500 ml reaction vessel, heated to 75°C, and kept at that temperature for three hours. The isocyanate content of the reaction mixture was determined to be 0.51 percent.

Now, 118.4 g (10.4 equivalents) of polyether triol were added together with an additional 0.04 g of dibutyltin dilaurate catalyst and the reaction mixture was again heated at 75°C for three hours until no isocyanate could be detected in the mixture.

Finally, 13.2 g (0.27 equivalent) of isocyanato-alkoxysilane and 0.04 g of a dialkyltin dicarboxylate

catalyst commercially available under the tradename "Formrez UL 28" were added and the mixture was once more heated at 75°C for three hours until isocyanate could no longer be detected.

5 The reaction mixture was then filled into a metal can container under nitrogen and sealed for storage.

 The following Examples relate to the use of the prepolymers prepared by the preceding Examples
10 in the formulation of sealant compositions.

Example 10

 A sealant composition was prepared by combining 62.26 parts by weight of the prepolymer of
15 Example 1 and 0.34 part of dibutyltin diacetate in a planetary mixer and mixing for 20 minutes under nitrogen to exclude moisture.

 At this point, 2.83 parts of N-(beta-amino-ethyl)-gamma-aminopropyl trimethoxysilane, 0.63 g
20 of tris-(dimethylamino-methyl)phenol as an optional catalyst, 2.93 parts of xylene, and 1.57 parts of methanol were added and the new mixture was mixed for an additional 20 minutes. All of the ingredients added in this step were carefully dried to avoid the
25 introduction of moisture into the composition.

 Finally, 14.72 parts of dried carbon black and 14.72 parts of dried clay were added to the mixture, which was mixed for a further 20 minutes under a reduced pressure of 2500 Pa. The sealant
30 compounded in this manner was filled into sealant tubes.

 The resulting sealant contains only 4.5 percent by weight of solvent, so that shrinkage due to solvent evaporation after cure will not be more than
35 4.5 percent. The sealant does not sag. The cure rate for the sealant was 25 N/cm² at 2.7 hours, determined by a quick adhesion test described immediately below.

For testing quick adhesion, a 10 x 0.63 cm bead of sealant is extruded from a sealant tube onto a primed glass plate. Another primed glass plate is placed on top of the sealant bead. This assembly is
5 sprayed with water and allowed to cure at room temperature for one hour, then immersed in a water bath at 25°C for four minutes. The plates are then separated by pulling in a plane perpendicular to the plane of the bead 2.7 hours after assembly time. The curing
10 rate is recorded in N/cm^2 at the elapsed time.

Example 11

A sealant comprising the prepolymer of Example 1 was formulated with a quaternary ammonium hydroxide
15 accelerator into a sealant composition suitable for fast room temperature curing.

As in Example 10, 61.62 parts of the prepolymer of Example 1 and 0.34 part of dibutyltin diacetate were combined in a planetary mixer and mixed prior
20 to addition of 2.80 g of N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, 0.62 part of tris-(dimethylaminomethyl)phenol as an optional catalyst, 2.90 parts of xylene, and 2.58 parts of benzyl-trimethylammonium hydroxide (40 percent in methanol).

25 After a further 20 minutes of mixing, 14.57 parts of dried carbon black and 14.57 parts of dried clay were added to the mixture and the formulation was again mixed under a reduced pressure of 2500 Pa for 20 minutes.

30 The sealant compounded in this manner was non-sagging. The curing rate in the aforementioned quick adhesion test was 53 N/cm^2 measured 2.7 hours after assembly, compared with a curing rate of 25 N/cm^2 for substantially the same material not con-
35 taining the quaternary ammonium hydroxide accelerator.

The lap shear strength of the composition was

tested by bonding two primed glass plates, each
2.5 x 10 x 0.63 cm with a sealant bead 2.5 cm long
by 0.63 cm wide by 0.8 cm high applied from a sealant
5 tes. The glass plates sandwich the sealant and com-
press its height to 0.85 cm. Samples are allowed to
cure at room temperature for seven days and are then
separated by pulling in a plane parallel to the plane
of the bead. In this test, the sealants of the example
10 developed a lap shear strength of 210 - 280 N/cm².

Example 12

A further sealant was prepared from the pre-
polymer of Example 7 as follows using the method of
15 compounding described in Example 10 above.

Namely, 61.28 parts of the prepolymer of
Example 7 are first combined with 0.33 parts of dibu-
tyltin diacetate catalyst and thoroughly mixed.
Thereafter 3.34 parts of N-(beta-aminoethyl)-gamma-
20 -aminopropyltrimethoxy silane, 0.61 part of tris-
-(dimethyl-aminomethyl)phenol, 2.90 parts of xylene,
and 2.56 parts of benzyltrimethylammonium hydroxide
(40 percent in methanol) are added and mixing is
continued for a further 20 minutes.

25 Finally, 14.49 parts of dried carbon black
and 14.49 parts of dried clay are added and the re-
sulting mixture is again mixed for 20 minutes under
partial vacuum.

The resulting sealant did not sag. Curing, as
30 measured by the quick adhesion test for the sealant,
was an average of 51 N/cm² 2.7 hours after assembly.
The beads of the sealant laid on glass developed
adhesion in seven days at room temperature.

Example 13

A sealant was prepared from the prepolymer of Example 1 using N-(beta-aminoethyl), N'-(gamma-trimethoxysilyl propyl)-ethylene diamine as a cross-linking agent and the method of compounding described in Example 10 above. 66.40 parts of the prepolymer of Example 1 were thoroughly mixed with 0.34 part of dibutyltin diacetate catalyst. Then, a mixture of 1.13 parts of N-(beta-aminoethyl), N'-(gamma-trimethoxysilyl propyl)-ethylene diamine, 1.51 parts of benzyltrimethylammonium hydroxide (40 percent in methanol), 1.36 parts of dried methanol, and 2.76 parts of dried toluene was added and mixing was continued for another 20 minutes. Finally 13.25 parts of dried carbon black and 13.25 parts of dried clay were added and the whole mixture was again mixed for 20 minutes under vacuum. The curing rate of the sealant so prepared, as measured by the quick adhesion test, was an average of 88 N/cm² 3.5 hours after assembly.

CLAIMS

1. A method of making a moisture-curable silicon terminated polymer, characterized in that a polyurethane prepolymer having terminal active hydrogen atoms is reacted with an isocyanato organosilane having a terminal isocyanate group and at least one hydrolyzable alkoxy group bonded to silicon.

2. A method as claimed in Claim 1, characterized in that the isocyanato organosilane has from one to three hydrolyzable alkoxy groups bonded to silicon.

3. A method as claimed in Claim 1, characterized in that the isocyanato organosilane is a compound of the formula

$$\text{OCN-R-Si-(X)}_m(\text{R}')_{(3-m)}$$

wherein R is a divalent organic radical, R' is hydrogen or alkyl having 1 to 4 carbon atoms, X is an hydrolyzable alkoxy group having from 1 to 4 carbon atoms, and m is an integer from 1 to 3.

4. A method as claimed in Claim 1, characterized in that the isocyanate organosilane is gamma-isocyanatopropyl triethoxysilane.

5. A method as claimed in any one of Claims 1 to 4, characterized in that the polyurethane prepolymer has terminal -OH, -SH, or -NH₂ groups.

6. A method as claimed in any one of Claims 1 to 4, characterized in that the polyurethane prepolymer has terminal -OH groups and is prepared by reacting an excess of a polyol with an organic polyisocyanate.

7. A method as claimed in Claim 6, characterized in that the polyol is a polyether polyol.

8. A method as claimed in Claim 7, characterized in that the polyether polyol is a polyether diol.

5 9. A method as claimed in Claim 8, characterized in that the polyether diol is a polyoxyalkylene diol.

10. A method as claimed in Claim 7, characterized in that the polyether polyol is a mixture of a polyether diol and a polyether triol.

10 11. A method as claimed in Claim 10, characterized in that the polyether diol is a polyoxyalkylene diol and the polyether triol is a polyoxyalkylene triol.

15 12. A method as claimed in any one of Claims 1 to 4, characterized in that the polyurethane prepolymer has terminal -OH groups and also has urea groups within the polymer chain and is prepared by reacting an excess of a mixture of a polyol and water with an organic polyisocyanate.

20 13. A method as claimed in Claim 12, characterized in that up to 25 percent of the total hydroxyl equivalents in said mixture are present in the water.

25 14. A method as claimed in Claim 6, characterized in that the polyol is a polyester polyol.

15. A method as claimed in Claim 14, characterized in that the polyester polyol is a polyester diol.

30 16. A method as claimed in Claim 15, characterized in that the polyester diol is a polyalkanolactone diol.

17. A moisture-curable silicon terminated organic polymer made by the method of any one of Claims 1 to 16.

35 18. A moisture-curable sealant composition comprising a moisture-curable silicon terminated organic polymer made by the method of any one of Claims 1 to 16 in combination with a least one filler.

19. A sealant composition as claimed in Claim 18, characterized in that it additionally comprises a curing catalyst for the silicon terminated organic polymer.

5 20. A sealant composition as claimed in Claim 19, characterized in that the catalyst is a quaternary ammonium hydroxide.

 21. A sealant composition as claimed in Claim 20, characterized in that the catalyst is benzyl-
10 trimethylammonium hydroxide.

 22. A sealant composition as claimed in Claim 18, characterized in that it additionally comprises an amino organosilane having at least one hydrolyzable alkoxy group bonded to silicon.

15 23. A sealant composition as claimed in Claim 22, characterized in that the amino organosilane is N-(beta-aminoethyl)-gamma-aminopropyl-trimethoxy silane.

 24. A sealant composition as claimed in Claim
20 22, characterized in that the amino organosilane is N-(beta-aminoethyl),N'-(gamma-trimethoxysilyl propyl)-ethylene diamine.

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